CHARACTERIZATION OF FRACTIONATED COAL LIQUIDS BY ^{13}C NMR AND FTIR SPECTROSCOPY

K. S. Seshadri and D. C. Cronauer

Gulf Research & Development Company
P. O. Box 2038
Pittsburgh, Pennsylvania 15230

INTRODUCTION

Coal liquids derived from solvent refined processes are complex mixtures of widely differing compounds with a high proportion of nonpolar aromatic compounds. The remainder is made up of polar compounds. A knowledge of these compounds is of importance for upgrading coal liquids and producing useful chemicals.

Computer-assisted Nuclear Magnetic Resonance and Infrared Spectroscopy have opened up new possibilities for a fairly detailed characterization of coal liquids. The present trend has been to depend more on ^{13}C NMR spectrum which is often congested with multiple signals. Direct observation of ^{14}N and ^{15}N nuclei and derivitization of coal liquids to silicon and fluorine derivatives followed by the observation on ^{29}Si and ^{19}F nuclei are on the horizon. The results of spectroscopic techniques, despite their sophistication, is of little value unless assisted by chromatographic methods capable of separating coal liquids into fractions that differ according to their chemical functionality.

Several chromatographic separation schemes are described in literature including SARA(1) and SESC.(2) In the latter technique the coal liquid is eluted from silica gel as the stationary phase with a sequence of solvents. We have expanded upon the analysis of combining SESC and spectroscopic techniques. Painter and Coleman(3) have examined the IR spectra of fractions of whole coal liquid obtained by SESC. However, more detailed structural information can be obtained when the whole coal liquid is first separated into light, middle and heavy distillate and bottoms followed by SESC separation and spectroscopic analysis. We have taken this approach, and the results on middle and heavy distillate cuts are reported here.

EXPERIMENTAL

The coal liquid used in this work was from the Ft. Lewis SRC-II facility (Tacoma, WA). The nominal run conditions with Powhatan No. 5 coal were 455°C, a space time of 60 min, and a hydrogen pressure of 1250 psi. The distillate yield (C_5-900°F) was about 40%, and the conversion of organic matter to pyridine solubles about 95%. The liquid was distilled into light distillate (C_5-380°F), middle distillate (380-550°F), heavy distillate (550-900°F), and residue (>900°F). Further separation of these fractions was by SESC(2) using Fisher S-662 silica gel of 60-200 mesh.

The ^{13}C NMR spectra of the fractions were recorded on a Varian FT-80A spectrometer. The solvent, $CDCl_3$, was used as a field-frequency lock, and chemical shifts are in ppm downfield from internal TMS. Spectra of some of the fractions were obtained with Cr(III) acetylacetonate and by suppressing nuclear Overhausser enhancement. Infrared spectra were recorded on a Nicolet Model 7199 Fourier transform spectrometer. Each spectrum was obtained by the co-addition of 100 interferograms at 2 cm^{-1} resolution and as thin films between KBr windows.

RESULTS AND DISCUSSION

The relative quantities of the middle and heavy distillate (MD, HD) fractions are given in Table I along with the elemental analysis of the first four HD fractions. The ^{13}C NMR and FTIR spectra of individual fractions are examined in the following sections to demonstrate the effectiveness of combining these two spectroscopic techniques with chromatographic separation.

Fraction 1MD (50.5% of Middle Distillate)

The ^{13}C NMR and FTIR spectra of this fraction are shown in Figures 1 and 2, respectively. Aromatic ring C-C vibrations result in IR absorptions near 1600 cm^{-1} and 1500 cm^{-1}. The relative intensity of the former depends on the nature of substitution on the ring. Here, the 1600 cm^{-1} band is of low intensity (vide infra) and the 3300 cm^{-1} region is flat, indicating that this fraction is composed of nonpolar aromatic compounds.

Certain features of the carbon spectrum, in particular multiple signals between 124.0-127.0 ppm, among which the signal at 125.7 ppm being most intense, suggest that naphthalene and alkyl naphthalenes are the dominant nonpolar compounds. The signals due to quaternary carbons are in the 132.0-137.0 region with a prominent signal at 135.1 ppm. The shielding of bridgehead or methyl-bearing carbon atoms in 1,8-dimethyl, 2,3-dimethyl, and 2-methyl naphthalenes is 135.2 or 135.4 ppm.[4] Therefore, a substitution pattern is established by the signal at 135.1 ppm and the IR spectrum is in agreement with this pattern. Out-of-plane hydrogen vibrational frequencies in alkylbenzenes in the 900-670 cm^{-1} region correlates well with the number of adjacent hydrogen atoms in the ring, and this correlation is also applicable to naphthalene.[5] Bands at 735 cm^{-1}, 780 cm^{-1}, and 805 cm^{-1} can be assigned to 4, 3, and 2-adjacent hydrogen wagging vibrations. The signals at 25.6 ppm, 21.5 ppm, and 19.2 ppm in the carbon spectrum are due to methyl carbons in 1,8-DIMeN, 2-MeN, and 1-MeN, respectively.[4]

The signals at 14.0, 22.0, 29.0, and 32.0 ppm are due to short-chain alkanes. The signal at 14.2 ppm is definitely a doublet, and the less intense of the doublet along with the signal at 20.9 ppm could be assigned to methyl carbons in 1,2-dimethylnaphthalene. Tetralin and homologs of tetralin are also possible, accounting for signals near 29.0 ppm and 23.0 ppm.[6]

Fraction 2MD (3.0% of Middle Distillate)

The carbon and the IR spectra of this fraction are shown in Figures 3 and 4, respectively. This fraction, has a very low population of sp^3 carbons. In addition, the carbon spectrum has a signal at 118.9 ppm, suggesting a structure with carbon atoms in the vicinity of an oxygen nuclei. Since the IR spectrum has no evidence for phenolic compounds, aromatic ether is a possibility. The signals at 118.9, 123.1, 129.7, and 157.3 ppm and their relative intensities favor diphenyl ether. The other signals at 141.2, 128.7, 127.2, and 127.1 ppm have been assigned to biphenyl. About 62% of this fraction is diphenyl ether and the balance is biphenyl.

The signals in the IR spectrum also support the presence of diphenyl ether and a high aromaticity of the fraction. The intense signal at 1238 cm^{-1} is due to asymmetric -C-O-C- stretch. In aromatic ethers, the C-O bond has double bond character due to resonance and, therefore, higher force constant than aliphatic C-O bond.[5] The signal due to the ether linkage, therefore, appears about 200 cm^{-1} higher than in aliphatic ethers. Other features of the IR spectrum are in agreement with the low population of sp^3 carbons.

Fraction 3MD (8.7% of Middle Distillate)

The carbon and the IR spectra of this fraction are shown in Figures 5 and 6, respectively. The IR spectrum has a broad absorption due to hydroxyl stretching near 3300 cm^{-1} with a narrower band at 3409 cm^{-1}. They are due to free and hydrogen-bonded NH groups and hydrogen-bonded phenolic hydroxyl groups. Therefore this fraction has phenolic and pyrrole-type compounds.

To understand the spectra of this and the subsequent fraction, reference is made to a library of carbon and IR spectra of alkyl phenols and indoles available in literature.[7,8,9]

The shielding of carbon nuclei in phenols bearing the -OH group extends from 155.0-152.0 ppm, and the exact location depends on the position of the methyl substitution. The carbon spectrum of this fraction has signals in the 153.5-151.0 ppm range, suggesting the presence of 2-, 2,5-, and 4-methylphenols. Signals around 15.5 and 15.2 ppm support this conclusion. A strong band at 752 cm^{-1} in the IR spectrum can be correlated with the vibrations of four adjacent unsubstituted aromatic H atoms. The band at 805 cm^{-1} correlates with two adjacent hydrogen wag or 4-methylphenol.

Other types of compounds that can be expected in this fraction are indoles and benzofurans.[2] The shielding of quaternary carbons in benzofuran and methylbenzofurans are in the 155.0-154.0 ppm range. Here this region has no absorptions. Moreover, furans and arylethers in our experiments are eluted along with nonpolar aromatics. Several features of the carbon spectrum agree well with indole and methylindoles. Part of the aromatic region of the carbon spectrum can be divided into five regions: (1) 130.0-126.9 ppm, (2) 124.2-119.6 ppm, (3) 116.6-113.5 ppm, (4) 111.1-108.7 ppm, and (5) 103.0-100.3 ppm. Many of the signals in these five regions are due to indoles. The signals in the fourth and the fifth regions are particularly diagnostic of indoles. They are due to carbons with an intervening carbon to nitrogen. The signals in the second region are due to carbons in the six-membered ring of the indoles and, since the shielding of three of them can be expected in this region, this region is congested. Indoles, at least those for which shielding data are available,[8] do not contribute to the third region, and signals in this region are due to phenolic compounds. The shielding of one of the quaternary carbons in indoles falls in the first region and that of the other quaternary carbon is near 136.0 ppm. The spectrum shown in Figure 5 was obtained with a short pulse delay. Therefore, the contribution to the intensity in the first region as well as the region around 136.0 ppm is marginal. Nevertheless, the first region has numerous signals, and they are indeed from protonated carbon atoms of phenolic compounds. Judging from the intensity distribution in the carbon spectrum, phenolic and the pyrrolic compounds are approximately in equal amounts.

In the saturated region of the spectrum, a strong signal is observed at 14.0 ppm. This signal is due to CH_3 carbons, and part of its intensity could be due to the CH_3 carbon in 2-methylindole. This is a reasonable structure since in the corresponding fraction of HD, carbazole has been recognized, and opening up of an aromatic ring could result in alkylindoles and possibly 2-methylindole.

Fraction 4MD (23.7% of Middle Distillate)

The carbon and the IR spectra of this fraction are shown in Figures 7 and 8, respectively. The broad absorption in the 3300 cm^{-1} region of the IR spectrum is due to hydroxyl stretching vibration. The band maximum is at 3320 cm^{-1} and it drops to the base line at almost 3600 cm^{-1}. The broad absorption is primarily due to hydrogen-bonded phenolic-hydroxyl groups. Bands due to N-H stretching vibrations also appear in this region of the spectrum. However, the carbon spectrum of this fraction has no absorption around 110.0 or 102.0 ppm, ruling out appreciable amounts pyrrolic nitrogen. Therefore, phenolic compounds are the major constituents of this fraction.

The aromatic region is again divided into appropriate regions to understand the types of phenolic compounds, namely: (1) 156.0-151.0 ppm; (2) 140.0-139.0 ppm; (3) 130.0-127.0 ppm; (4) 123.0-120.0 ppm; (5) 117.2-115.9 ppm; and (6) 114.0-111.0 ppm. The shielding of C-2 (C-6) in phenol is 115.4 ppm. However, in m-cresol relative to phenol, the shielding of C-2 is shifted downfield by about 0.8 ppm; whereas, due to the <u>para</u> shielding effect of the CH_3 group, C-6 is shifted upfield to

112.5 ppm. m-Cresol, 3,5-dimethylphenol (3,5-DMP), and similar structures are responsible for the sixth region. The signal at 116.4 ppm can also be associated with these structures. In the two model compounds mentioned above, the shielding of carbon bearing the CH_3 group is at 139.3 and 139.0 ppm, respectively, and indeed two signals at 139.8 and 139.5 ppm are observed in the second region. The shielding of CH_3 carbons in m-cresol, 3,5-DMP, and p-cresol are not perturbed by the -OH group relative to the corresponding CH_3 carbons in methylbenzenes. The signals at 21.2 and 20.4 ppm suggest phenols with $-CH_3$ groups, one or two carbons away from the carbon bearing the -OH group. The first region can be subdivided into a singlet at 155.3 and a group of signals from 154-153 ppm. The shielding of C-OH carbon in phenol, m-cresol, 3,5-DMP is 155.0, 155.0 and 155.4 ppm, respectively. In ortho- and para-cresols, in 2,6-DMP, in 2-isopropylphenol, and in 2-tert-butylphenol, the shielding is shifted upfield by about -2.8 ppm. Therefore, part of the signals in the first group suggest the presence of these compounds. The shielding of other quaternary carbon atoms in o-cresol and 2.6-DMP is at 124.0 and 123.8 ppm, and signals with reduced intensity are observed near 124.0 ppm. Most of the intensities in the fifth region are due to two signals at 115.4 and 115.5 ppm. These signals are due to C-2 and C-6 protonated carbons and are arising from ortho- and para-cresols. Other diagnostic signals in the carbon spectrum are those near 15.5 ppm. The shielding of CH_3 carbon in the immediate vicinity of the OH group is shifted upfield relative to that of CH_3 carbons in toluene or m-xylene. Therefore, these signals are in agreement with the presence of 2,6-DMP and o-cresol. Shielding of other carbons in the structures mentioned above are around 120.0 and 129.0 ppm, and resonances have been observed in these regions.

Most of the prominent signals have been assigned to specific carbons in phenolic compounds. However, the unassigned signals around 146.3, 136.4, and 28.7 ppm are conspicuous. The signal at 28.7 ppm is intense and could be due to CH_3 carbons in 2-t-butylphenol. The signal at 136.4 ppm could also be associated with this structure. The signals around 146.3 ppm are assigned to quaternary carbons in diphenols. These assignments are tentative.

The carbon spectrum has assisted in deciding the location of methyl groups relative to the OH group. Additional proof and other pertinent information can be derived from the IR spectrum. The C-C vibration of an aromatic ring can be divided into 1600 cm^{-1} and 1500 cm^{-1} vibrations. The 1500 cm^{-1} region has several components, depending on the number of alkyl substitutions. More importantly, the 1600 cm^{-1} vibration is less intense than the 1500 cm^{-1} vibrations. However, with electron donor or acceptor groups, the intensity of the former vibration is enhanced due to the dipole moment change provided by different groups. The 1600 cm^{-1} band of this fraction is more intense compared to the same band in the spectrum of fraction 1, due to the OH group on the aromatic ring.

The OH deformation and C-O stretch frequencies in the case of phenols are close to each other and, therefore, they are strongly coupled.[5] They fall above 1100 cm^{-1} and extend up to 1330 cm^{-1}. A broad absorption is observed in this region due to the presence of numerous phenols. However, a well resolved signal is observed at 1156 cm^{-1} which is probably due to C-O stretch in a 3-substituted phenol.

The signals in the 650-850 cm^{-1} region are due to out-of-plane H vibrations and ring bending vibrations. The band at 696 cm^{-1} has been assigned to ring puckering mode and the other three bands to out-of-plane C-H vibrations. The signal at 776 cm^{-1} can be assigned to a phenol with three adjacent H atoms. In the structures that have already been considered, two adjacent H atoms and an isolated H atom are possible. The wagging vibrations of these hydrogen atoms are responsible for the bands at 856, 836, and 816 cm^{-1}.

In this fraction we have identified cresols and xylenols as major components. A small percentage of phenol cannot be ruled out. This fraction has 14% of phenolic oxygen estimated from the carbon spectrum. Among phenols, cresols and xylenols are in equal amounts--40% and 48%, respectively--and about 10% of phenol itself.

Fraction 5MD (2.4% of Middle Distillate)

The carbon spectrum of this fraction is shown in Figure 9. An unusual feature of the carbon spectrum, is the signals at 156.0-159.0 ppm. These signals along with signals in the 152.0-146.0 ppm, an isolated signal at 136.7 ppm with satellites is a strong indication that pyridine and methylpyridines are present in this fraction. The carbon spectrum also suggests the presence of carbon nuclei in the vicinity of the OH group. The signals at 115.8 and 112.3 ppm are diagnostic of phenolic compounds. Further upfield there are prominent signals at 107.2, 107.0, 103.1, 102.7 ppm. These are probably due to carbon nuclei in the complexes of phenolic and basic nitrogen compounds.

Fraction 1HD (50.7% of Heavy Distillate)

This fraction, which is yellow in color, turns cloudy on refrigeration, suggesting the presence of waxy materials. The carbon spectrum has appropriate signals to substantiate the presence of alkanes. No attempt was made to assign the other signals to specific carbon nuclei. However, the spectrum has two signals around 111.5 ppm and a group around 156.0 ppm which are diagnostic of dibenzofuran (DBF).[10] Since more than one signal has been observed in these regions, DBF and alkyl derivatives of DBF are possible. Subject to this assignment, the weight percent of oxygen in this fraction was obtained from the carbon spectrum (0.32%) agreeing fairly well with the results of elemental analysis (0.54%). This fraction has an equal amount of sulfur, that could be present as dibenzothiophene.

Fraction 2HD (24.5% of Heavy Distillate)

The carbon spectrum of this fraction is shown in Figure 10. Unlike the carbon spectrum of the previous fraction, only a limited number of signals are observed, partly due to the high aromaticity (92.5%) of the fraction. Signals at 131.9, 130.1, and 130.9 ppm are due to quaternary carbons. The former two have been assigned to phenanthrene and the latter to pyrene. The other signals in the spectrum support these structures. Weak signals in the spectrum are due to hydroaromatic hydrocarbons derived from phenanthrene and pyrene.

The signal at 131.9 and 130.9 ppm are of equal intensity. However, four carbons of pyrene contribute to the intensity of the latter signal; whereas, two carbons of phenanthrene are at 131.9 ppm. Therefore, phenanthrene is twice as abundant as pyrene in this fraction.

The low frequency region (900-700 cm^{-1}) of the IR spectrum is in agreement with the carbon spectrum. Bands in this region arise from C-H wagging vibration. The vibrational frequencies of C-H bonds approximately parallel to the long axis of the molecule are near 740 cm^{-1}, and those of C-H bonds approximately perpendicular to the long axis are near 850 cm^{-1}.[11] Also due to angular condensation, a characteristic band is observed between these two regions. The bands at 744 cm^{-1} and 736 cm^{-1} are assigned to C-H bonds parallel to the long axis in phenanthrene and pyrene, and those at 860 cm^{-1} and 840 cm^{-1} are assigned to CH bonds perpendicular to the long axis. The band at 810 cm^{-1} which is characteristic of C-H bending vibration in angular polynuclear aromatic hydrocarbons supports the two structures that we have selected to assign signals in the carbon spectrum.

Fraction 3HD (13.2% of Heavy Distillate)

The carbon and the IR spectra of this fraction are shown in Figures 11 and 12, respectively. The IR spectrum has a broad absorption at 3300 cm^{-1} and a narrower band at 3410 cm^{-1}, suggesting that this is analogous in composition to fraction 2MD; that is, it has a structure with N-H linkage and phenolic compounds. The carbon spectrum has signals at 110.6, 119.20, 120.22, 123.2, 125.7, and 139.6 ppm. These match exactly with the resonances observed for carbazole.[10] This fraction is very aromatic (93.1%) and, therefore, it is not surprising that one of the major components of this fraction is carbazole. The signals at 139.6 and 123.2 ppm appear with reduced intensity because they arise from quaternary carbons.

From the intensity of the signal at 110.6 ppm, the percentage of nitrogen is 2.3% compared to 3.27% from the elemental analysis. Therefore, most of the nitrogen in this fraction is accounted for by carbazole. Singnals near 115.8 ppm and weak shoulders to signals at 110.6 ppm and 120.2 ppm suggest the presence of hydroxy aromatic compounds. However, in the absence of shielding data for hydroxy aromatic compounds with three or more rings, assignment of these signals to specific carbon nuclei has not been possible.

Fraction 4HD (7.8% of Heavy Distillate)

The carbon and the IR spectra of this fraction are shown in Figures 13 and 14, respectively. The aromaticity of this fraction is much less (61.5%) than that of the previous fractions.

The aromatic region of the spectrum is divided into four regions: (1) 157.0-150.0 ppm; (2) 147.0-132.0 ppm; (3) 132.0-125.0 ppm; and (4) 120.0-109.0 ppm. The first region has three well defined signals at 156.9, 156.2, and 154.7 ppm. The broad absorption near 3300 cm^{-1} and the enhanced intensity of 1600 cm^{-1} relative to the 1450 cm^{-1} band in the IR spectrum indicate the presence of hydroxy aromatic compounds. The shielding of carbon-bearing OH groups in phenols are in the 155-152 ppm region, whereas in naphthols and 9-hydroxyphenanthrol, the shielding of the corresponding carbon is shifted upfield to 153.0-151.0 ppm in $CDCl_3$. If this trend should continue, the carbon spectrum, for example, of hydroxybenzanthracene, should have a signal near 151.0 ppm. Therefore, signals around 156.0 ppm are somewhat surprising. This fraction has 1.3% nitrogen, and if this nitrogen is present as basic nitrogen, hydroxy basic nitrogen heterocyclics, like hydroxypyridines, have carbons with shieldings near 156.0 ppm. This possibility is unlikely since hydroxypyridines and 8-hydroxyquinoline do not have carbons with chemical shifts near 114.3 ppm. Therefore, the nitrogen is present as pyrrolic nitrogen, although there are no pronounced evidences both in the carbon and the IR spectrum for the N-H linkage.

The IR spectrum has two well defined signals at 730 cm^{-1} and 905 cm^{-1} which are characteristic of C-H wagging vibration in polynuclear aromatic hydrocarbons with four or more condensed rings. The 730 cm^{-1} is a singlet, except for a weak shoulder suggesting that PNAs are sparsely substituted. Therefore, the major portion of the sp^3 carbons are in the hydroaromatic rings, and the hydroaromatic structures account for the group of signals in the second region. The signals in the third and the fourth region arise from carbons well removed from the OH group and those in the immediate vicinity of the OH group, respectively.

These observations suggest that the hydroxyaromatic compounds in this fraction have partially hydrogenated three or more condensed rings. It is likely that in such structures the shielding of aromatic carbon bearing the OH group is near 156.0 ppm and not at 151.0 ppm as in 9-phenanthrol.

SUMMARY

The results presented here amply demonstrate that the combined results of ^{13}C NMR and FTIR spectroscopy can provide a wealth of information not only about the functional groups in coal liquids, but also details regarding the structure of moelcules carrying these groups.

The first two fractions of SESC are homogeneous; they contain nonpolar aromatic compounds. Included in this category are the diaryl ethers, benzofurans, and benzothiophenes. The rest of the fractions are heterogeneous. All of them to a greater or lesser extent contain hydroxyaromatic compounds. However, fraction 3 is highly homogeneous, containing mainly phenolic compounds. The presence of phenolic compounds does not interfere with the identification of other functional groups in fractions 3 and 5 due to: (1) their low concentration and (2) high resolution of absorptions in the ^{13}C NMR spectrum. The type of functional groups in each fraction, according to the carbon and IR spectroscopic results are summarized in Table 2.

REFERENCES

1. Ruberto, R. G., Jewell, D. M., Jensen, R. K., and Cronauer, D. C., Advances in Chemistry Series, No. 151, Chapter 3, American Chemical Society, Washington, DC, 1976.

2. Farcasiu, M., Fuel 1977, 56, 9.

3. Painter, P. C., and Coleman, M. M., Fuel 1979, 58, 301.

4. Wilson, N. K., and Stothers, J. B., J. Mag. Resonance 1974, 15, 31.

5. Colthup, N. B., Daly, L. H., and Weberley, S. E., Introduction to Infrared and Ruman Spectroscopy, Academic Press, New York and London, 1964.

6. Seshadri, K. S., Ruberto, R. G., Jewell, D. M., and Malone, H. P, Fuel, 1978, 57, 111.

7. Johnson, L. F., and Jankowski, W. C., Carbon-13 NMR Spectra, Wiley-Interscience, New York, 1972.

8. Breitmaier, E., Haas, G., and Voelter, W., Atlas of Carbon-13 NMR Data, Heyden, Long-Philadelphia-Rheine, 1979.

9. Shrewsbury, D. D., Spectrochimica Acta 1960, 16, 1294.

10. Seshadri, K. S., Unpublished results.

11. Jones, R. N., and Sandorfy, C., The Application of Infrared and Raman Spectroscopy to the Elucidation of Molecular Structure, Chapter IV, Volume IX, in A. Weissburger, Technique of Organic Chemistry, Interscience, New York, 1956.

Table 1

FRACTIONS OF MIDDLE AND HEAVY DISTILLATE OF COAL LIQUID AND ELEMENTAL ANALYSIS OF HD

Fraction	Eluent	Wt% of MD
1	Hexane	50.5
2	Hexane + Benzene(15%)	3.0
3	Chloroform	8.7
4	Chloroform + Ether(4%)	23.7
5	Ether + EtOH(3%)	2.4
Losses (Volatiles)		11.7
		100.0

	Wt% of HD	C	H	O	N	S
1	50.7	90.60	8.11	0.54	0.00	0.54
2	24.5	92.18	5.91	0.31	0.10	0.47
3	13.2	81.92	7.16	3.69	3.27	0.23
4	7.8	82.25	7.40	5.54	2.03	0.12
5	2.9					
Losses	0.9					
	100.0					

Table 2

TYPES OF COMPOUNDS IN THE FRACTIONS OF MD AND HD

Fraction	Type of Compounds
1 and 2	Nonpolar aromatics, diaryl ethers, benzofurans, and benzothiophenes.
3	Mainly nonbasic N compounds; hydroxy aromatic compounds.
4	Hydroxy aromatic compounds.
5	Basic N compounds; hydroxy aromatic compounds.

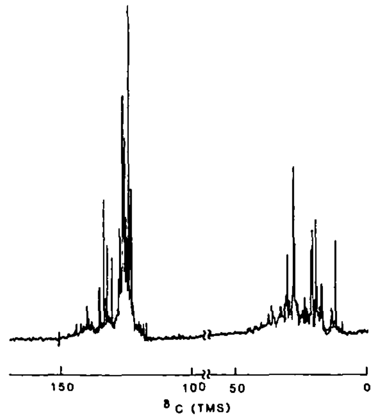

Figure 1 ^{13}C NMR Spectrum of Fraction 1MD

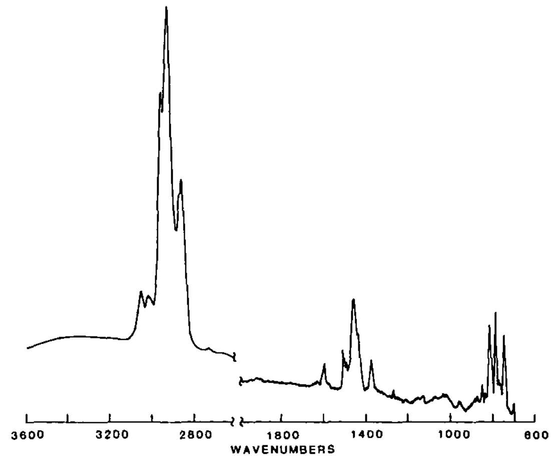

Figure 2 FTIR Spectrum of Fraction 1MD

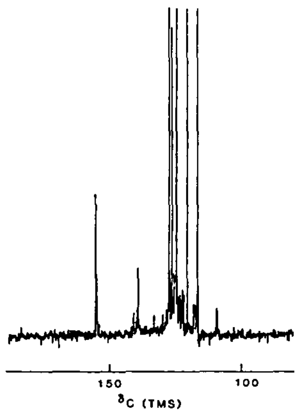

Figure 3 ^{13}C NMR Spectrum of Fraction 2MD

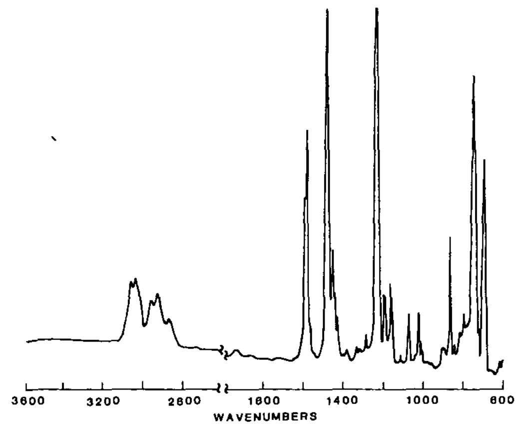

Figure 4 FTIR Spectrum of Fraction 2MD

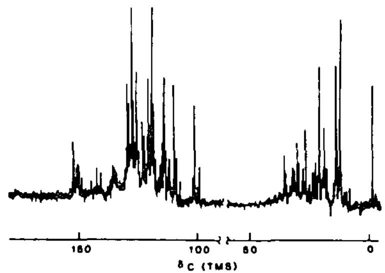

Figure 5 ^{13}C NMR Spectrum of Fraction 3MD

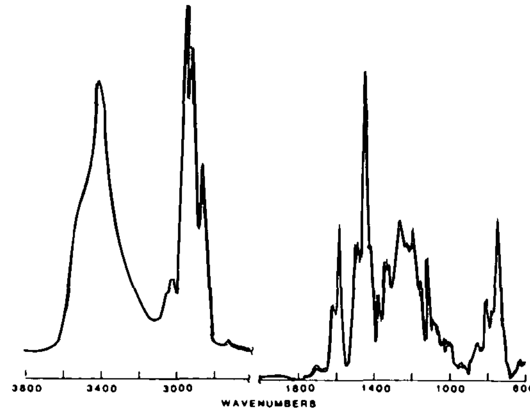

Figure 6 FTIR Spectrum of Fraction 3MD

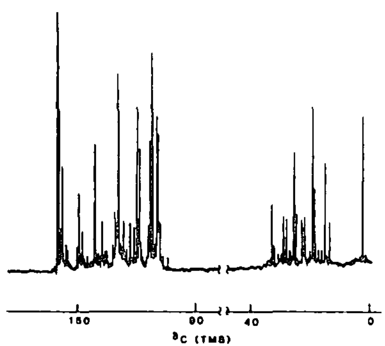

Figure 7 ^{13}C NMR Spectrum of Fraction 4MD

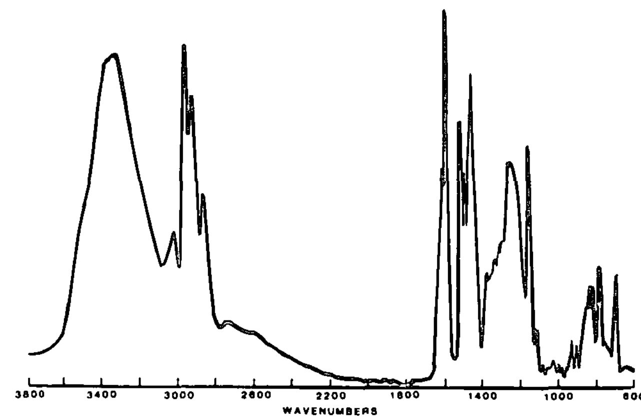

Figure 8 FTIR Spectrum of Fraction 4MD

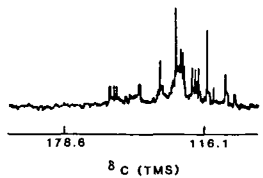

Figure 9 ^{13}C NMR Spectrum of Fraction 5MD

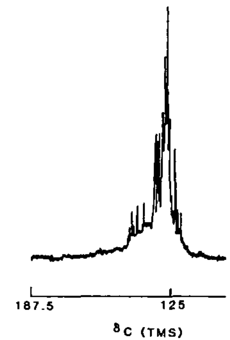

Figure 10 ^{13}C NMR Spectrum of Fraction 2HD

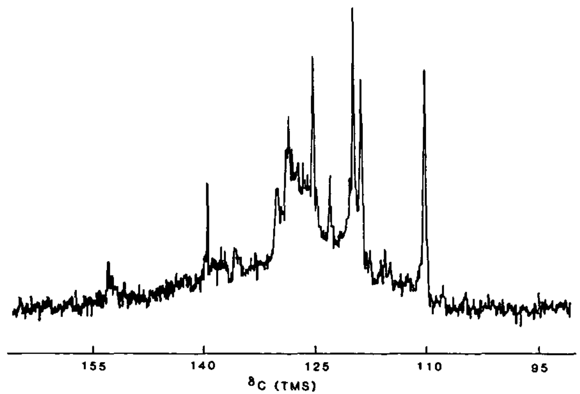

Figure 11 ^{13}C NMR Spectrum of Fraction 3HD

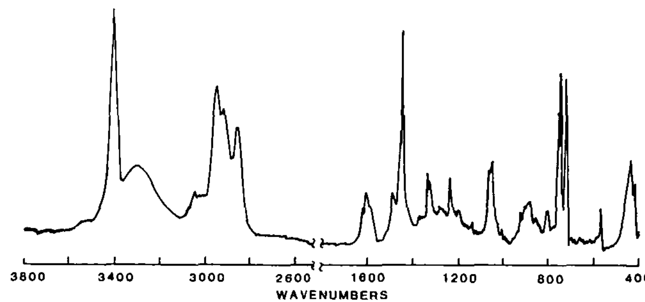

Figure 12 FTIR Spectrum of Fraction 3HD

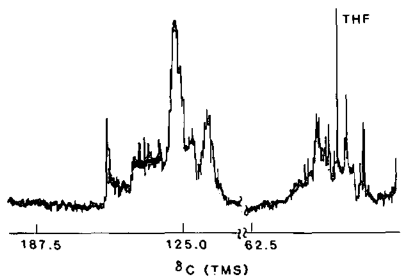

Figure 13 ^{13}C NMR Spectrum of Fraction 4HD

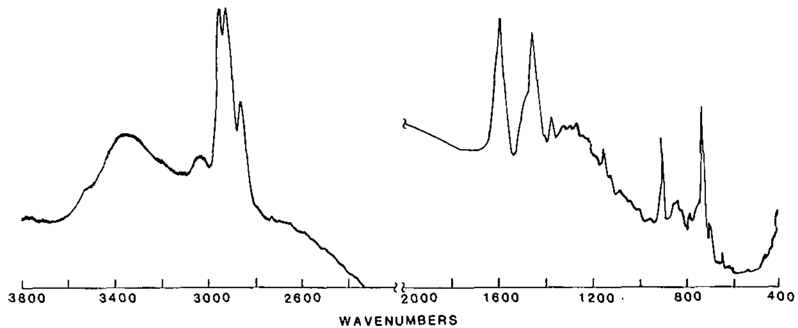

Figure 14 FTIR Spectrum of Fraction 4HD